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(54) Title: **PHOSPHATE BINDER AND ITS PREPARATION**

(57) Abstract: **An inorganic binder having calcium silicate sites which are connected the one with the other by alumina-silica phos-  
phate bounds.**

**WO 03/031366 A1**

Phosphate binder and its preparation

5 The present invention relates to an inorganic binder, most precisely to an inorganic phosphate binder.

Inorganic phosphate binder have already been proposed in the past.

10 For example in a previous patent application WO9903797 in the name of Metal Chemical and Haji Anas, a polymeric matrix is disclosed, said matrix comprising a binder formed by mixing an alkali metal silicate aqueous solution with a powder comprising silico-aluminous reactive raw materials. A polymerization time of  
15 more than one hour is however necessary for reaching a sufficient hardening of the matrix.

It has also been proposed in US 6,139,619 to form a binder by mixing a water soluble silicate with a water soluble amorphous inorganic phosphate glass in an aqueous medium. The hardening of the binder requires the removal of water by a  
20 heat treatment.

In US 4,375,551, an acid solution is prepared by mixing  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  with phosphoric acid, said acid solution being then mixed with calcium silicate. The so  
25 obtained binder has after hardening poor mechanical strength.

The present invention has for subject matter a binder which can be sufficiently hardened within a term of less than 10 minutes and which has excellent mechanical properties.

30 The inorganic binder of the invention is characterized by calcium silicate sites which are connected the one with the other by alumina-silica phosphate bounds.

Advantageously, the calcium silicate sites are calcium meta silicate sites having a substantially acicular nature with a length/diameter ratio from 2/1 to 50/1, advantageously from 3/1 to 20/1.

- 5 Preferably, the calcium meta silicate sites has an average length from 10 $\mu$ m to 10mm, advantageously from 50 $\mu$ m to 5 mm.

The calcium silicate sites act preferably as cross-linking sites for alumina-silica phosphate bounds.

10

According to an embodiment, the alumina-silica phosphate bounds have a ratio  $Al_2O_3/SiO_2$  ranging from 0.3 :1 and 10 :1, advantageously from 0.6 :1 and 6 :1.

- 15 According to an advantageously embodiment, the weight ratio calcium silicate sites/alumina-silica phosphate bounds is comprised between 0.1 and 1.1, advantageously between 0.3 and 0.9, preferably between 0.4 and 0.7.

The invention relates also to a product comprising at least a binder according to the invention and at least one filler and/or reinforced material.

20

The invention relates also to a kit for the preparation of inorganic binder composition according to the invention, said kit comprising :

- 25 - a container of bag containing a water insoluble calcium silicate, and  
- one or more containers or bags containing compounds for preparing an acid alumina-silica phosphate solution, the pH of said solution measured at 20°C being less than 1.5, advantageously less than 1, preferably less than 0.5.

- 30 A further subject matter of the invention is a process for the preparation of a binder according to the invention, in which water insoluble calcium silicate particles are mixed with an acid alumina-silica solution at a temperature lower than 50°C, said acid alumina-silica solution having a pH less than 2, advantageously less than 1.5,

for example comprised between 0.1 and 1.5, preferably comprised between 0.5 and 1.5. The acid pH is advantageously obtained by using phosphoric acid or an acid mixture containing at least phosphoric acid. Preferably, substantially only phosphoric acid is used as mineral acid, most preferably as acid for lowering the pH of the solution to less than 2.

The calcium silicate particles are advantageously calcium meta silicate particles having a substantially acicular nature with a length/diameter ratio from 2/1 to 50/1, advantageously from 3/1 to 20/1.

The calcium meta silicate particles have preferably an average length from 10 $\mu$ m to 10mm, advantageously from 50 $\mu$ m to 5 mm.

According to a preferred embodiment, the calcium silicate particles act as cross-linking sites for alumina-silica phosphate bounds. It seems also that the presence of insoluble calcium silicate particles catalyzes the formation of alumina-silica phosphate bounds.

In the process of the invention, the alumina-silica phosphate solution has advantageously a ratio  $Al_2O_3/SiO_2$  ranging from 0.3 :1 and 10 :1, preferably from 0.6 :1 and 6 :1.

For example, the weight ratio calcium silicate particles/alumina-silica phosphate solution is comprised between 0.1 and 1.1, preferably from 0.3 and 0.9, most preferably between 0.4 and 0.7.

In the process of the invention, a filler and/or a reinforced material is mixed with the calcium silicate particles before being mixed with the acid alumina-silica phosphate solution and/or a filler and/or a reinforced material is mixed to the mixture calcium silicate/alumina - silica phosphate solution, before or during its hardening.

Preferably, the hardening of the binder is carried out at a temperature comprised between 0°C and 50°C, possibly under pressure.

Examples of fillers or reinforced materials which can be mixed with the binder before its preparation, during its preparation, before its hardening or during its hardening are :

- waste materials, such as finely divided waste material, for example fuel ashes, fly ashes, buildings waste materials, etc.
- flake-like materials such as mica, etc.,
- 10 - silica sand, silica flour,
- coloring agents or materials, such as inorganic coloring agents, pigments, etc.
- cellulose and/or protein base fibers, such as natural fibers, flax, chip, straw, hemp, wool fibers, etc.
- synthetic fibers, such as organic synthetic fibers, inorganic synthetic fibers,
- 15 - such as polyesters, polypropylene, glass and ceramic fibers, etc.
- natural and synthetic organic base waste materials, such as saw dust, rice husk, straw and recycled organic waste,
- natural fibers of mineral origin,
- natural material, possibly treated (for example heat treated), such as perlite,
- 20 - vermiculite, etc.
- etc.

Additives can be added to the binder before its preparation, during its preparation, before its hardening or during its hardening, such additives are for example :

- 25 - foaming agents, such as water peroxide, organic peroxide, etc.
- viscosity regulating agent, such as superplasticizer
- material for improving the impermeability or the water repulsion such as lignosulfonates and silica fume
- etc.

30

The binder of the invention is prepared by using an acid alumina-silica phosphate solution, said solution is advantageously prepared by reacting aluminum oxide

powder (size advantageously lower than 50 $\mu$ m, preferably lower than 30 $\mu$ m, for example from 5 to 25  $\mu$ m) with a purity of more than 95%, preferably more than 99%, silica powder (size advantageously lower than 50 $\mu$ m, preferably lower than 30 $\mu$ m, for example from 10 to 25  $\mu$ m) with a purity of more than 95%, preferably  
5 of more than 99%, and phosphoric acid as an aqueous phosphoric acid or in presence of an aqueous medium. The phosphoric acid has preferably a purity of more than 95%, most preferably of more than 99%. Phosphoric acid is available in various concentration. Preferably, the phosphoric acid will be a phosphoric aqueous solution with a phosphoric acid concentration of more than 75%,  
10 preferably of more than 85%. Preferably, the silica powder is first mixed with the phosphoric acid and then the alumina particles are added.

The acid alumina-silica phosphate solution contains possibly some other acids, such as organic acid, strong mineral acid, etc, however, in this case, the content of  
15 such acid will preferably be less than 10% of the phosphoric acid content of the solution.

Instead of using aluminum oxide, it is possible to use aluminum phosphate, aluminum hydroxide, etc. However, aluminum oxide is preferred.  
20

Instead of using silica, preferably precipitated silica particles, it is possible to use waste material issuing from glass bottles.

Possibly the aqueous phosphoric acid solution contains other solvents, such as  
25 alcohol, etc.

When a foamed product is desired, more water or solvent will be used for decreasing as much as possible the viscosity.

The acid alumina silica phosphate solution has advantageously a pH lower than 2,  
30 preferably lower than 1.

It has been observed that when using silica particles for the preparation of the acid alumina phosphate solution with a pH lower than 2, most preferably lower than 1, the dissolution of alumina particles was improved. The presence of solubilized  $\text{SiO}_2$  in the acid solution was also improving the formation of the bounds when  
5 adding the water insoluble calcium silicate particles. Even, if some calcium silicate particles are solubilized due to the low pH, some calcium silicate particles remains insoluble, due for example to the increase of pH to a value comprised between 3 and 6.

10 The binder of the invention is suitable for preparing product having a light weight (such a weight from 70 to 140  $\text{kg/m}^3$ ) or a heavy weight (such as weight of 2,000  $\text{kg/m}^3$  or even more).

Products of the invention have high mechanical properties, such as compression  
15 strength of more than  $40\text{N/mm}^2$ , bending strength of more than  $10\text{ N/mm}^2$ , etc.

Products of the invention can be used as insulating materials (as panels, sheets, granules, etc), fire protection material, heat protection material, chemical protection material, buildings material (such as bricks, concrete, etc.), for making molds,  
20 shaping, casting and moldings products, tiles, roofing sheet, etc.

Details and characteristics of the invention will appear from the description of the following examples.

25 In said examples, the following products have been used :

WATER : water with a low calcium/magnesium content (less than 100 ppm)

$\text{SiO}_2$  : precipitated  $\text{SiO}_2$  particles with an average size of 10-15 $\mu\text{m}$  – purity of 99%

30

$\text{Al}_2\text{O}_3$  : powder with an average particle size of 10-15  $\mu\text{m}$  – purity of 99%

Phosphoric acid : aqueous solution containing 90% phosphoric acid .

Calcium silicate : calcium meta silicate powder, water insoluble, acicular nature, length of 1 mm, diameter 100 $\mu$ m.

5

#### Examples of Binders

The binders have been prepared by adding SiO<sub>2</sub> particles to phosphoric acid. After dissolution of the SiO<sub>2</sub> particles, Al<sub>2</sub>O<sub>3</sub> particles were added. An acid alumina  
10 silica phosphate aqueous solution was so prepared. The pH of said acid solution was then measured at 20°C. Possibly some water was added.

To said acid solution, calcium silicate particles was added. 5 to 10 minutes after the addition of calcium silicate particles, the binder was hardened. Said hardening  
15 was made at room temperature.

The following table gives the composition of the binders prepared.



Binder	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub> (g)	35	16	21	13.6	46.2	60	182	130.8	97.2	233
Al <sub>2</sub> O <sub>3</sub> (g)	24	23	13	50.8	30.8	60	136.5	21.8	58.1	46.6
Phosphoric acid (g)	141	141	167	123	135.6	180	182	87.4	184.7	350.4
Molar Ratio SiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> Of the solution	0.4 3	0.2	0.2	0.19	0.59	0.58	1.73	2.62	0.92	1.15
Calcium silicate (g)	120	100	150	60	100	150	200	140	240	310
Water (ml)	80	40			25	60	118	21	71	65
pH of the acid solution	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
pH of the solution after addition of the calcium silicate	1	0.5	1	0.5	0.5	1.5	1	1	1.5	1.5
Appearance of the mixture after the addition of the calcium silicate (LS, S-D, P)	LS	LS	S-D	S-D	P	LS	LS	S-D	P	P

\* : LS = Liquid suspension / S-D = Semi-dry / P = Pasty

- 5 In the process of the invention, the amount of calcium silicate added to the acid silica alumina phosphate solution is such that the weight ratio calcium silicate / SiO<sub>2</sub> present in the acid solution is advantageously greater than 1, preferably greater than 1.5, most preferably greater than 2, for example comprised between 1 and 5, advantageously comprised between 1.5 and 3.5.

Examples of products of the invention

The binder n°2 which is liquid after its preparation was mixed with various additives and/or filler.

The following table gives the different additives and fillers used.

Product n°	1	2	3	4	5	6
Binder (part by volume)	1	1	1	1	1	1
Additive (Part by volume)	H <sub>2</sub> O <sub>2</sub> 0.13	Silica Fume 0.42	Aluminum powder 0.12	Super Plasticizer 0.15	Ligno-Sulfonate 0.13	Quartz 0.54
Filler (part by volume)	Vermiculite 0.33	Straw 3 parts	Fly ash 0.52	Chip 1.22	Flax Fiber 0.75	Silica Flour 0.25
Appearance of the product	Foam, low density	Low density	Foam Low density	Low density	Low density	Heavy density

WHAT I CLAIM IS :

- 5 1. An inorganic binder having calcium silicate sites which are connected the one with the other by alumina-silica phosphate bounds.
2. The binder of claim 1, in which the calcium silicate sites are calcium meta silicate sites having a substantially acicular nature with a length/diameter ratio from  
10 2/1 to 50/1, advantageously from 3/1 to 20/1.
3. The binder of claim 2, in which the calcium meta silicate sites has an average length from 10 $\mu$ m to 10mm, advantageously from 50 $\mu$ m to 5 mm.
- 15 4. The binder of anyone of the claims 1 to 3, in which the calcium silicate sites act as cross-linking sites for alumina-silica phosphate bounds.
5. The binder of anyone of the preceding claims, in which the alumina-silica phosphate bounds have a ratio  $Al_2O_3/SiO_2$  ranging from 0.3 :1 and 10 :1,  
20 advantageously from 0.6 :1 and 6 :1.
6. The binder of anyone of the claims 1 to 5, in which the weight ratio calcium silicate sites/alumina-silica phosphate bounds is comprised between 0.1 and 1.1, advantageously between 0.3 and 0.9, preferably between 0.4 and 0.7.
- 25 7. A product comprising at least a binder according to anyone of the claims 1 to 6 and at least one filler.
8. A kit for the preparation of inorganic binder composition according to anyone of  
30 the claims 1 to 6, said kit comprising :
  - a container of bag containing a water insoluble calcium silicate, and

- one or more containers or bags containing compounds for preparing an acid alumina-silica phosphate solution or containing an alumina-silica phosphate solution, the pH of said solution measured at 20°C being less than 1.5, advantageously less than 1, preferably less than 0.5.
- 5
9. A process for the preparation of a binder according to anyone of the claims 1 to 6, in which water insoluble calcium silicate particles are mixed with an acid alumina-silica phosphate solution at a temperature lower than 50°C, said acid alumina-silica phosphate solution having a pH less than 2, advantageously less than 1.5, preferably comprised between 0.5 and 1.5.
- 10
10. The process of claim 9, in which the calcium silicate particles are calcium meta silicate particles having a substantially acicular nature with a length/diameter ratio from 2/1 to 50/1, advantageously from 3/1 to 20/1.
- 15
11. The process of claim 10, in which the calcium meta silicate particles have an average length from 10µm to 10mm, advantageously from 50µm to 5 mm.
- 20
12. The process of anyone of the claims 9 to 11, in which the calcium silicate particles act as cross-linking sites for alumina-silica phosphate bounds.
- 25
13. The process of anyone of the preceding claims, in which the alumina-silica phosphate solution has a ratio  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ranging from 0.3 :1 and 10 :1, advantageously from 0.6 :1 and 6 :1.
- 30
14. The process of anyone of the claims 9 to 13, in which the weight ratio calcium silicate particles/alumina-silica phosphate solution is comprised between 0.1 and 1.1, advantageously between 0.3 and 0.9, preferably between 0.4 and 0.7.
15. The process of anyone of the claims 9 to 14, in which a filler is mixed with the calcium silicate particles before being mixed with the acid alumina-silica

phosphate solution and/or a filler is mixed to the mixture calcium silicate/alumina – silica phosphate solution, before its hardening.

16. The process of any one of the claims 9 to 15, in which the hardening of the  
5 binder is carried out at a temperature comprised between 0°C and 50°C.

17. The process of anyone of the claims 9 to 16, in which the binder is hardened under pressure.

10 18. The process of anyone of the claims 9 to 17, in which the water insoluble calcium silicate is a calcium meta silicate having a substantially acicular nature with a length/diameter ratio from 2/1 to 50/1, advantageously from 3/1 to 20/1.

19. The process of claim 18, in which the calcium meta silicate has an average  
15 length from 10µm to 10mm, advantageously from 50µm to 5 mm.

20. The process of anyone of the claims 9 to 19, in which the amount of calcium silicate added to the acid silica alumina phosphate solution is such that the weight ratio calcium silicate / SiO<sub>2</sub> present in the acid solution is greater than 1, preferably  
20 greater than 1.5, most preferably greater than 2.

21. The process of claim 20, in which the amount of calcium silicate added to the acid silica alumina phosphate solution is such that the weight ratio calcium silicate / SiO<sub>2</sub> present in the acid solution is comprised between 1 and 5, advantageously  
25 comprised between 1.5 and 3.5.

22. The process of anyone of the claims 9 to 21, in which the acid silica alumina phosphate solution is prepared by mixing a silica and/or alumina mixture with an acid consisting substantially only of phosphoric acid, and by adding possibly to the  
30 formed acid solution further silica and/or alumina.

## INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C04B28/34

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 4 504 555 A (PRIOR WILLIAM L ET AL) 12 March 1985 (1985-03-12) claim 1; examples 4,14	1-8  9-14,16, 18,19,22
X A	US 3 179 527 A (VUKASOVICH MARK S ET AL) 20 April 1965 (1965-04-20)  column 1, line 12-17; claim 4	1-4, 9-12,16, 18,19,22
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A	EP 0 507 463 A (FOSECO INT) 7 October 1992 (1992-10-07) example 1	

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

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